Carbon Nanoforms for Photovoltaics: Myth or Reality?

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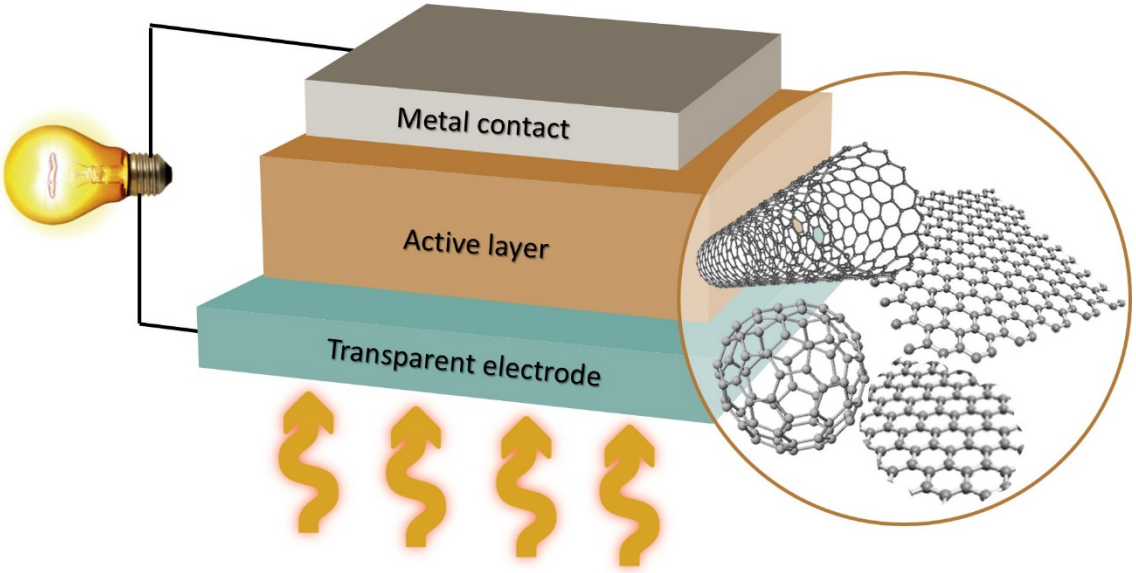
http://www.ucm.es/info/fullerene/

TOC

Carbon nanoforms, namely fullerenes, CNTs, graphene and graphene quantum dots reveal appealing properties to be used as interesting active materials for the preparation of photovoltaic devices. The experimental findings evidence that far from being a myth, these carbon materials are becoming a reality with remarkable energy conversion efficiencies.



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1. Introduction

Energy represents nowadays the most important problem for Mankind. Actually, combustion of carbon-based materials, namely fossil fuels such as petroleum derivatives, natural gas and coal are the origin of the CO_2 production, which is responsible, in a great extent, for the rapid environmental degradation undergone by our planet. On the other hand, carbon owing to its inherent capacity for hybridizing atomic orbitals is able to generate a wide variety of allotropic forms. Therefore, it is not surprising that this element, and particularly some recently well-known carbon nanostructures, could play an important role in finding a solution to the global energetic demand.

The principal known carbon nanoforms are, in a chronological order, fullerenes, carbon nanotubes, graphene and graphene quantum dots.[1] Although many other forms of carbon are known (endohedral fullerenes, carbon nanohorns, carbon nanoonions, peapods, or even the recently controversial carbyne,[2] to name a few), we will focus our attention on the main known carbon nanoforms based on their availability and suitability for their use in PV purposes. Fullerenes, with a distinctive symmetrical carbon cage structure formed by C$sp^{2,3}$ atoms, have been the object of intense research since their discovery over three decades ago.[3] In contrast to zero dimensional (0D) fullerenes having around 1 nm of diameter, single-wall (SWCNT) and multi-wall (MWCNT) carbon nanotubes present a cylindrical 1D geometry and structurally belong to the family of fullerenes.[4] Carbon nanotubes present a length to diameter ratio of up to 28,000.000:1, reaching lengths of up to several millimetres. In contrast to fullerenes, CNTs are not homogeneous materials exhibiting different lengths, widths and structures resulting from the different modes in which, formally, a graphene sheet can be wrapped around a chiral vector to form the cylindrical CNT shape. According to the indices of the chiral vector, *armchair*, *zigzag* and *chiral* nanotubes can be formed, although usually, these three species can be found together in the same sample. Nowadays, the selective synthesis of CNTs has been, however, drastically improved and relatively pure materials are affordable.

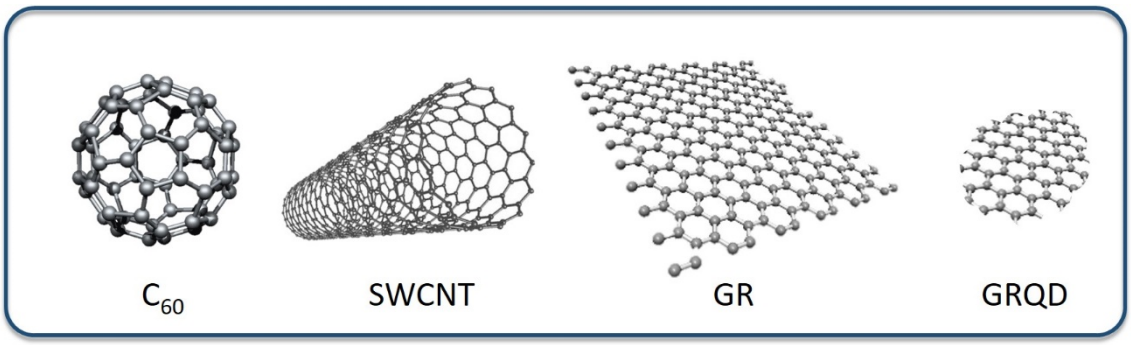

Figure 1. Chemical structures of the main carbon nanoforms, namely fullerene C_{60}, a single wall carbon nanotube, graphene and a graphene quantum dot

Graphene is an atomically thin mesh of carbon atoms arranged in a honeycomb pattern.[5] Actually, carbon atoms in graphene are so tightly packed that even helium atoms cannot pass through. Furthermore, single-layer graphene can have a surface area as large as 2600 m^2/g. Although single-layer graphene is prepared by physical means (epitaxial graphene, CVD or reduction of silicon carbide), chemical methods such as exfoliation of graphite by solvents (Coleman's method) or mechanical methods typically lead to the so-called few-layer graphene, which has been extensively studied in the last years. This also applies to the most recent graphene quantum dots, which, interestingly, exhibit some different properties from that of pristine graphene such as, for instance, fluorescence. [6]

Although fullerenes, and in particular C_{60} with its singular spherical molecular shape, have been used as a benchmark for establishing the chemical reactivity and properties of these carbon-based species, their singular geometric and electronic distribution have afforded unanticipated and surprising new chemically modified fullerenes structures with amazing properties. These former studies have significantly facilitated and guided the study of the chemical reactivity of structurally more complex CNTs and graphene where size, shape and composition are not homogeneous and where, in contrast to fullerenes, the edge features can significantly modify their reactivity and properties.

The aim of this essay is just to bring to the attention of the readership the role that the most abundant, available and well-known nanoforms of carbon, namely fullerenes, carbon nanotubes and graphene, including the most recent graphene quantum dots, are currently playing in the field of organic photovoltaics.[7] Whether these new carbon-based materials are suitable or not for PV applications is still an open question since they have to compete with efficient PV materials such as silicon or the most recent perovskites. The answer to this question will try to be unraveled along this essay, which eventually will clarify if the use of these carbon-based materials for PV is eventually just a myth or a reality.

2. The beginning: Plastic Solar Cells in the EU

To the best of my knowledge, the first EU project devoted to photovoltaics (PV) involving the molecule of C_{60} as the active material was in the end nineties. At that time, fullerenes were among the most studied molecules by the scientific community. Actually, it was in 1996 – just eleven years after the discovery of [60]fullerene – when H. Kroto, R. E. Smalley and R. Curl received the Nobel Prize in Chemistry for the discovery of Fullerenes.[8] No doubt, the study of the generation/formation and the physicochemical properties of fullerenes resulted in the discovery of new carbon nanoforms like carbon nanotubes (CNTs) and graphene (GR) among others.

The EU project entitled: "Molecular plastic solar cells" (Ref.: JOR3-CT98-0206 of the 4th Framework Programme) was coordinated by Niyazi Serdar Sariciftci, recently arrived from Alan Heeger's lab in Santa Barbara University (UCSB) (California), to Johannes Kepler University of Linz (Austria). The project involved other different institutions from Europe and Israel (David Faiman, Ben-Gurion University of Negev; Mats Andersson, University of Goteborg; Olle Inganas, Linköping University; René Janssen, TU Eindhoven; Kees Hummelen University of Groningen;

Maurizio Prato and Michele Maggini, University of Padova; and Nazario Martín, Complutense University, as company partner QSEL Linz which became Konarka Austria later in 2001).

The aim of this Joule project was to demonstrate that efficiencies of devices based on this plastic technology could reach values for the energy conversion efficiencies beyond 3 % on the laboratory scale (1 cm^2) and to investigate techniques for fabrication of large area cells using polymer printing.

Previous studies had shown that C_{60}, the soccer ball-shaped fullerene molecule, significantly assists the process of photogeneration. Due to its high electron affinity, C_{60} represented an excellent electron acceptor, while conjugated polymers in their undoped, semiconducting state act as electron donors. Therefore, these conjugated polymer/acceptor blends were an important type of plastic solar cells under investigation in this project. Actually, it was announced in the project proposal that "Plastic solar cells have the potential for a revolutionary impact on the electricity supply for consumer goods".

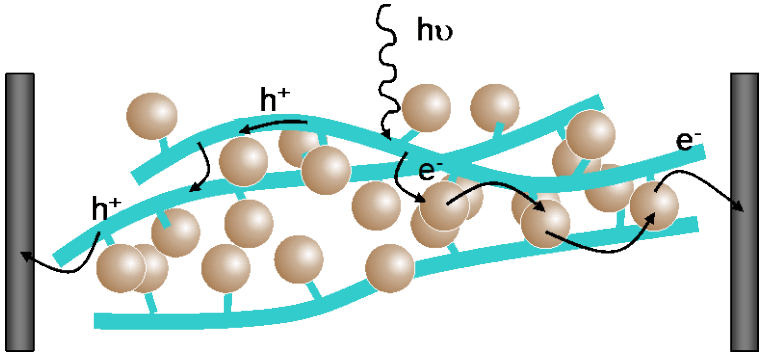

Figure 2. Original figure in the EU project entitled: "Molecular plastic solar cells" (Ref.: JOR3-CT98-0206 of the 4th Framework Programme) for the double cable concept, representing the units of C_{60} covalently linked to the semiconducting polymer

The main objectives of this project were reasonably achieved. The main compounds prepared were based on the so-called "double-cable approach" in which suitably functionalized fullerene derivatives were covalently connected to different semiconducting polymers (Poly(*p*-phenylene vinylene), PPV derivatives). These new cells were referred to as "Bulk Heterojunction Solar Cells" (BHSC) since domains of donor (polymer) and acceptor (fullerene) electroactive systems were randomly distributed in the bulk material. This donor/acceptor segregation, in the right extent, was found to be essential for the device efficiency. However, many other open questions remained since then. These issues are mostly related with a variety of aspects such as light absorption, morphology, charge separation, stability, processing, encapsulating, etc. stemming from the differenced steps involved in the PV process, namely light absorption, excitons generation (basically a neutral electron/hole pair), separation of excitons into charges and, eventually, the transport and collection of charge carriers to the electrodes. Most of these concepts have later been addressed and improved in a great extent.[9] More important, however, was the fact that this first project allowed gathering some research groups with different backgrounds from Europe that, along the next coming years, were able to construct a solid network on this "crazy idea" of fabricating solar cells from fullerene-based materials.

Furthermore, it proved that these outstanding nanoforms of carbon, namely fullerenes were appealing and promising materials for application in PV devices.

3. The state of the art

The Sun is a giant natural nuclear fusion reactor, being the most powerful source of energy available in our Solar System. Therefore, the development of highly efficient, renewable and sustainable strategies for using Sun energy is currently an important challenge in science. Actually, the energy received from Sun, calculated as 120 000TW (5% ultraviolet; 43% visible and 52% infrared), surpasses that needed in our planet for one year by several thousand times.[10]
Since the first silicon-based device prepared by Chapin in 1954 exhibiting an efficiency around 6%,[11] different semiconducting materials (inorganic, organic, molecular, polymeric, hybrids, quantum dots, etc.) have been used for transforming Sun light into chemical energy. Nowadays, silicon-based solar cells are have achieved power conversion efficiencies (PCE) of around 25% for crystalline Si solar cells, and around 15% for amorphous and microcrystalline silicon.[12] However, the harsh experimental conditions and high energy required for the fabrication process has fuelled the development of new alternative/complementary materials. Thus, inorganic salts such as copper indium gallium selenide or cadmium telluride have shown PCE values over 20%.[13] However, despite these inorganic materials are competitive with Si in economic and efficiency values, they exhibit important drawbacks such as a remarkable toxicity and low abundance of In and Te elements.
More recently, organolead trihalide perovskites ($CH_3NH_3PbX_3$, X=Cl, Br, I)[14] have shown outstanding PCE values (over 20%) in a record time.[15] Nevertheless, perovskites-based devices have important drawbacks, being the most important one that concerned with their stability under ambient conditions. It is important to note, however, that some nanoforms of carbon are currently being used in the perovskites-based device fabrication as electron transporting materials or even replacing the TiO_2 in the device design.[16]

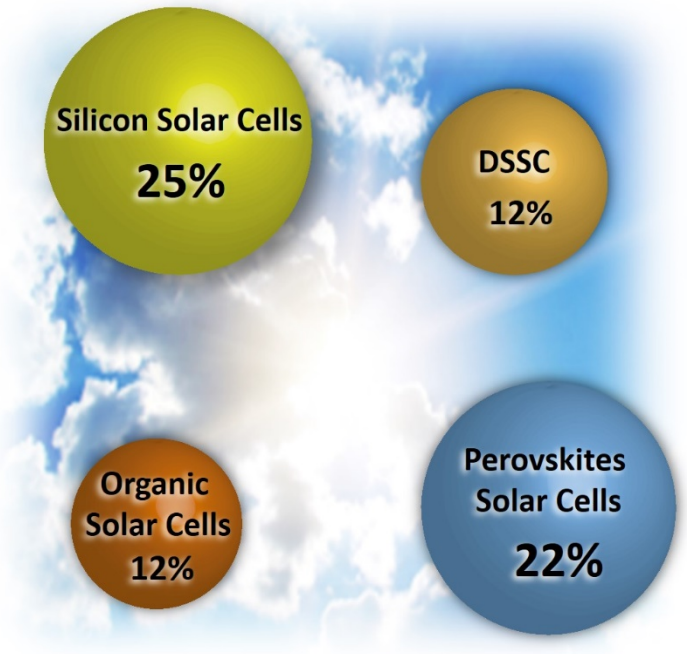

Figure 3. Main types of solar cells and the record efficiencies achieved so far.

Dye-sensitized solar cells (DSCs) represent another important class of PV devices, which are able to convert solar radiation into electricity in an efficient and low-cost manner. These devices are typically formed by a light-harvesting sensitizer (inorganic or organic dye) anchored to a high surface area of mesoporous semiconductor film.[17] Record efficiencies over 12% in solid state devices have been measured with ruthenium-complex sensitizers on laboratory scale devices.[18] Again, problems associated to Ru metal such as availability as well as a rather complex synthesis and purification prevent a future large-scale power production of DSSCs. Metal-free organic sensitizers are a valuable alternative since they are synthesized at low price and their absorption properties can be finely tuned by molecular design. Reports of new organic dyes with efficiencies surpassing 10% have been reported with a donor-π-acceptor molecular scheme.[19]

4. Carbon nanoforms for Organic Photovoltaics: Some significant achievements

The natural scenario for the use of known carbon nanoforms is in the so-called Organic Solar Cells (OSC) where they behave as active materials in the preparation of the devices. Some of the most significant features and PV properties of these materials have been gathered in some recent reviews [7,20] and some relevant issues are presented in the following sections.

4.1. Fullerenes as active materials

Carbon nanomaterials, namely fullerenes, nanotubes, graphene as well as graphene quantum dots have been studied, in a different extent, for a variety of applications in devices for energy conversion such as solar cells. In the following, some of the most significant achievements of these representative nanoforms of carbon in the field of energy conversion are presented.

In general, organic materials are appealing for PV due to some key such as the ability for solution processing, affording flexible, lighter and cheaper PV devices. These aforementioned features confer a singularity to these organic materials when compared with the most commonly used silicon.

In the field of all-organic solar cells, the most widely studied materials have been those based on blends of electron-donor semiconducting polymer and chemically modified fullerene as the electron-acceptor component. In this regard, based on their electronic (moderate electron-acceptor) and geometric (singular sphere shape) properties, fullerenes have proved to be the ideal electron conducting (n type) material to form a bicontinous phase network with π-conjugated polymers (Figure 4).[21]

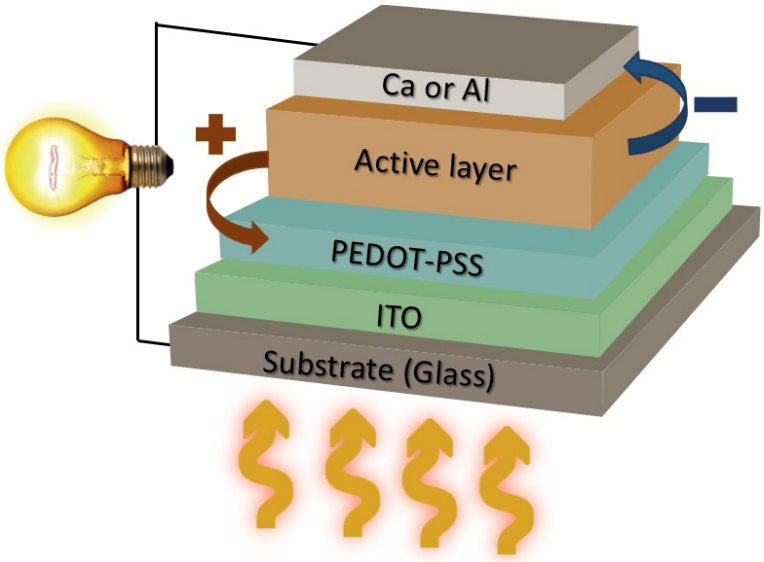

Figure 4. Sandwich-like architecture for an organic solar cell. Semiconducting polymers and chemically modified fullerenes are blended in the appropriate ratio to form the photovoltaic active layer

No doubt, the most widely used and best known fullerene derivative for PV devices is [6,6]-phenyl-C61 butyric acid methyl ester ([60]PCBM) [22]. Since its first application in solar cells [23], it has been by far the fullerene of choice, together with its more light absorbing related derivative [70]PCBM. Both C_{60} and C_{70} PCBM derivatives have been used as benchmark materials for testing new organic molecules or carbon-based materials.[24] In this regard, since it is currently well-established the strong impact of the fullerene derivative LUMO energy level for controlling the photovoltaic parameter Voc (open circuit voltage) of the fabricated device, a wide variety of many other chemically modified fullerenes have been synthesized with significantly different LUMO energy values.[25 Among the different modified fullerenes prepared so far, diphenylmethanofullerenes (DPMs) prepared in our group represent another successful type of methanofullerenes endowed with two alkyl chains to improve the solubility of the acceptor in the blend.[26] Interestingly, whereas the reduction potential for DPMs is the same as that for PCBM, an increase for the Voc of around 100 mV over PCBM has been observed which has been accounted for by the difference in the density of states occupancy for both fullerenes.[27]

The aforementioned fullerene monoadduct derivatives as well as others like those stemming from indene (ICMA) and *ortho*-quinodimethane (*o*QDMC), typically show small shifts (< 100 meV) of the LUMO level. This value can be finely tuned just by linking either electron-acceptor or electron-donor organic addends to the fullerene sphere. Remarkably higher Voc values have been obtained, however, by means of the polyaddition of organic addends to the fullerene cage, thus forming the so-called bis-adducts (see ICBA in Figure 5). Actually, a number of different bis-adducts have been reported in the literature and, due to the saturation of two double bonds which raises the LUMO level, most of them exhibit improved Voc values and, therefore, better efficiencies.[28]

The cyclopropanation reaction to higher fullerenes, namely C_{70}, to form [70]PCBM analogues is synthetically more complex than for C_{60} provided that up to four differently reactive double bonds are present in C_{70}. Indeed, the lower symmetry and the presence of several reactive

double bonds are responsible for the formation of regioisomeric mixtures. On the positive side, C_{70} has a stronger absorption in the visible region of the electronic spectrum as a consequence of the loss of symmetry in C_{70}. Actually, the extinction coefficient of [70]PCBM is nearly five times that of [60]PCBM at 600 nm and around 20 times at 475 nm.[29] Thus, [70]PCBM has been widely used as a molecule of choice for the preparation of more efficient polymer solar cells. In fact, the highest verified efficiency determined so far in a BHJ solar cell, with an internal quantum efficiency approaching 100% has been reported for [70]PCBM.[30] Other larger fullerenes such as, for instance [84]PCBM, have been prepared as a mixture of isomers showing low solubility and significantly lower conversion efficiencies (Figure 5).[31]

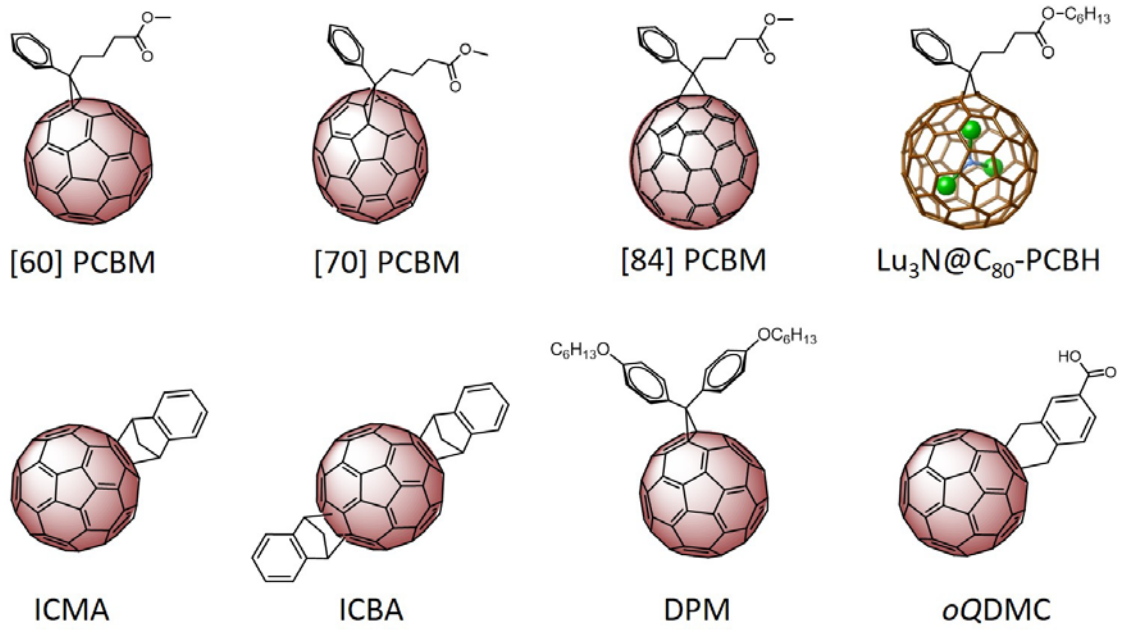

Figure 5. Chemical structures of some of the most used fullerene derivatives as n-type materials for organic photovoltaics.

Although not mentioned before, endohedral fullerenes (fullerenes bearing an atom, molecule or cluster in the inner cavity of the carbon cage) have shown possibilities to be used as n-type materials in organic photovoltaics. Actually, the first molecule tested, a $Lu_3N@C_{80}$ derivative, mixed with poly-3-hexylthiophene (P3HT/$Lu_3N@C_{80}$-PCBH) exhibited a competitive efficiency of over 4.0 %, slightly surpassing that obtained for empty [60]PCBM as a reference.[32] It is important to remark, however, that although endohedrals show a wide range of redox potentials depending on the contained chemical species (thus controlling the Voc), the low amounts available as well as their high cost have severely prevented their use in photovoltaics so far.

Since the former studies on fullerenes for BHJ photovoltaics, an impressive number of research groups have been engaged in this scientific hot topic, giving rise to a huge number of scientific papers in which the efficiency value has been systematically increased. However, and most important, these studies have led to a good understanding on those factors which control the different photovoltaic parameters and, eventually, the efficiency and stability of the cell. In this regard, several important review papers have been published along the last recent years.[33]

Heliatek company claimed at the beginning of 2013 that world record efficiency of 12 % had been achieved based on a standard sized cell of 1.1 cm². They used a combination of two

patented absorber materials able to convert light of different wavelengths, thus resulting a higher photovoltage and better efficiency. Although efficiencies up to 15% should be achieved for 2015, these results have not been reported so far by this company.

The highest efficiency value reported for a BHJ solar cell has been published in 2016 by the group of He Yan from the Hong Kong University of Science and Technology. The fabricated single-junction organic solar cells showed a record efficiency of 11.5%, which has been officially certified. This achievement has been noted as a major technological breakthrough in the renowned NREL chart of "best research-cell efficiencies." Actually, the same group has surpass their own record by introducing a non-halogenated hydrocarbon-based processing system that is not only more environmentally friendly but also yields cells with power conversion efficiencies of up to 11.7% (Figure 6).[34]

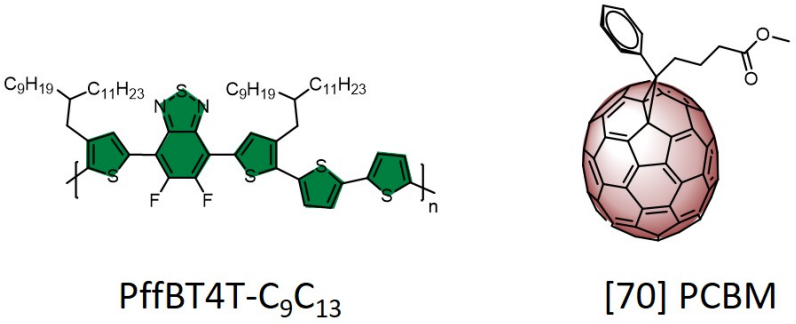

Figure 6. Chemical structures of the p-type semiconducting polymer and n-type fullerene derivative which blended in the right conditions afforded the highest record efficiency in BHJ solar cells.

No doubt, the progress in the field of BHJ solar cells will continue improving the efficiency values and the Heliatek's prediction will become a reality in a relatively near future. The efforts in improving the synthetic methods for obtaining better materials by design both in the p-type semiconducting polymers as well as in the n-type fullerene derivatives together with the better control in the fabrication processes have been the key issues for this relatively slow but consistent progress.

4.2. Carbon nanotubes

In contrast to the wide use of fullerenes for photovoltaics, CNTs have been significantly less employed for this purpose due to their different nature and properties. Despite the interest of CNT, they have serious problems to be used for practical purposes. The reason for this impediment stems from the way in which CNTs are produced resulting in a carbon material with low purity. As produced CNTs are formed by the complex mixture of the own CNTs – with different lengths, diameters and chirality – together with metal catalyst particles and amorphous carbon in different shapes and sizes. Actually, the selective synthesis of CNTs with a control on the diameter and chirality still represents a challenge for the scientific community.

Since photovoltaic devices formed by π-conjugated polymers and C_{60} derivatives have promise for cheap and sustainable practical applications, substitution of C_{60} with SWCNTs have been extensively explored. SWCNTs exhibit good properties as charge carriers and, in addition, they present a high absorption in the visible range, thus being in principle good active materials for harvesting photons to be transformed into excitons in the PV devices. Therefore, SWCNTs have

been blended with conjugated polymers to be used as the active layer in OSCs.[35] However, it is important to note that, despite PV effects were clearly observed, the resulting efficiency values resulted to be quite low. This low efficiency has mostly been accounted for by some limitations in the exciton generation and the charge separation and recombination processes.

The appropriate energy level alignment is also an important issue for the cell performance. In this regard, depending on their metallic or semiconducting nature, SWCNTs have bandgaps which strongly depend on their chiralities. These experimental observations have been supported by means of theoretical calculations which clearly show the different behavior of the metal and semiconducting SWNTs.[36] Thus, metallic SWNTs interact stronger with semiconducting polymer P3HT, resulting in a stronger charge transfer from the polymer to the SWNTs in the ground state. This process prevents in some extent the exciton dissociation and the eventual electron transfer to SWNTs. Therefore, it should be expected that semiconducting SWNTs in blends with semiconducting polymers result in better efficiencies in the devices, as it has been experimentally confirmed.[37]

A solar cell geometry able to maximize photocurrent by using polychiral SWCNTs while retaining high photovoltage, leading to efficient SWCNT−fullerene solar cells with average NREL certified and champion PCEs of 2.5% and 3.1%, respectively, has recently been reported. Interestingly, these cells exhibit a significant absorption in the near-infrared region of the solar spectrum.[38]

This new approach enhancing light absorption by combining [70]PCBM and polychiral semiconducting SWCNTs coupled with an open-circuit voltage maximized by careful interface and electrode selection has allowed to double the efficiency of SWCNT−fullerene solar cells. This finding is an important step forward since the ability of multiple chiralities to contribute efficiently to photocurrent is in contrasts to previous works suggesting single-chirality SWCNTs as a requirement for efficient PV devices. Furthermore, the absorption of these material in the near-infrared region of the solar spectrum paves the way to improve the efficiency of transparent and tandem solar cell architectures. In addition, the use of these carbon-based materials leads to PV devices with high thermal and chemical stability which, eventually, could remove the required encapsulation currently used in PV technologies.

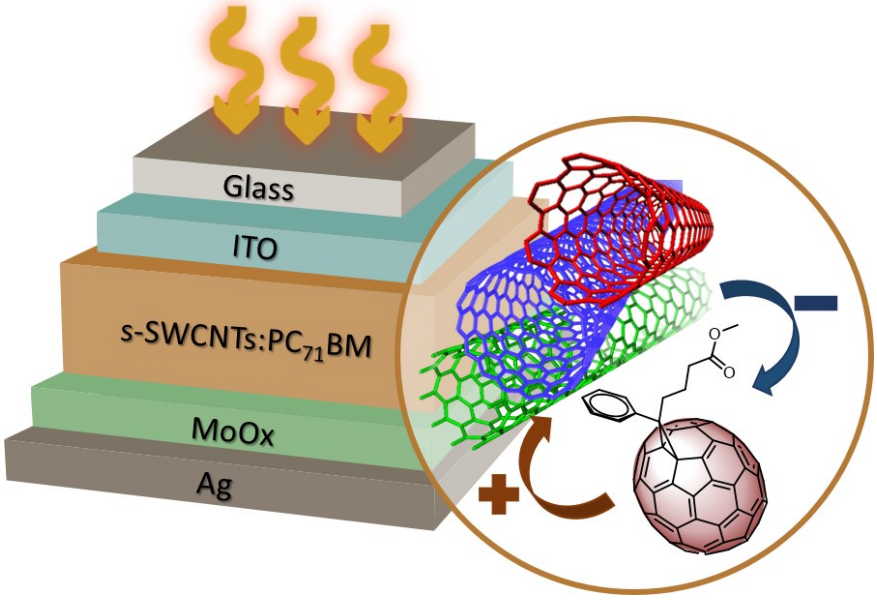

Figure 7. All-carbon materials (CNTs and [70]PCBM) as active materials and configuration for the photovoltaic solar cell (se reference 39).

In order to determine the use of CNTs in PV, a controlled placement of a single-walled CNT (SWNT) monolayer at four different positions in polymer-fullerene bulk-heterojunction (BHJ) solar cells has been reported.[39] This study demonstrated that SWNTs on the hole collection side of the active layer afford better energy conversion efficiency in the photovoltaic devices from 4 to 4.9% (under AM 1.5 G, 1.3 suns illumination). Although in this case the CNTs are not a part of the active material, this is the highest PCE value reported for polymer-based solar cells incorporating CNTs.

Another important application found for CNTs in OSCs is based in the remarkable high mobility of CNTs which make them excellent materials for improving the charge transport in PV devices. In this regard, due to the right energy level of the CNT or its presence providing high mobility channels from the active layer to the cell electrodes, the presence of CNTs has a favorable effect for improving the charge transport processes in the PV devices. This effect has experimentally been confirmed in OSCs where the addition of CNTs results in an improvement both in holes and electron transport. As a representative example, the active layer formed by fullerene with a semiconducting polymer in OSCs undergoes a quite significant increase in the electron transport when SWCNTs are blended with the active layer.[40] Related results have been observed when using [60]fullerene and SWCNTs in SWNT/fullerene/P3HT blends, affording higher photovoltaic parameters (FF and J_{SC}) and, eventually, better PV performances.[39]

Despite the aforementioned drawbacks, CNTs, based on their good electrical conductivity, high charge transport ability, high mesoporosity and electrolyte accessibility, are, however, quite appealing for application as, for instance, electrode materials for high-performance supercapacitors. This topic is, however, out of the scope of this essay. [41,42]

4.3. Graphene

Graphene (G) exceeds to CNTs in charge mobility being among the best conducting materials. Therefore, graphene is expected to find realistic applications in PV devices. However, attending to the nature of pristine graphene, it would not meet the required criteria to be of interest for PV active materials since it has a zero-bandgap. However, there are several methodologies which have allowed the band-gap opening in a controlled manner. Thus, for instance, when graphene is oxidized into GO, the bandgap is opened and it can be controlled by means of the oxidation degree.[43] Thus, functionalized GO has been applied as active layer in OSCs and a variety of papers have been published in this regard.[44] Interestingly, a different and efficient method to open the bandgap of graphene is to utilize the quantum confinement effect. Thus, the so-called graphene “quantum dots” (GQDs) have also been synthesized either by top-down and bottom-up approaches with a certain degree of control on their sizes and electronic properties.

Since GO can be chemically modified with a variety of functional groups, this strategy has been employed for preparing more appropriate GO derivatives for PV purposes. As a representative example, functionalized GO with phenyl isocyanate transformed the typical hydrophilic GO

surface into a hydrophobic surface.[45] This chemical change allowed blending the resulting modified graphene with semiconducting poly(3-octylthiophene) (P3OT) to form the active layer material in the bulk heterojunction (BHJ) OSC. Interestingly, after annealing (160 ºC, 20 min), a significantly better device performance was observed, reaching promising efficiency values as high as 1.4 %. This experimental finding has been accounted for by removing the functional groups from graphene, thus improving the polymer crystallinity. This result paves the way to the use of graphene as an alternative electron acceptor carbon-based material for PV devices.

Other related functionalized graphenes have also been developed like, for instance, with aniline-functionalized graphene as well as with graphene quantum dots (GQDs) acting as electron acceptors by blending with a semiconducting electron donor polymer such as P3HT. The system bearing the modified graphene showed, however, lower efficiency values (0.65 %) than those shown by the related blends formed by aniline functionalized graphene quantum dots (GQDs) and P3HT with efficiencies surpassing 1 % values (1.14%).[46]

The above two examples clearly reveal, as happened with fullerenes in the earlier times, that these carbon nanostructures clearly show their interest in the field of organic photovoltaics and still there are plenty of room for further improvement in the use of graphene and graphene quantum dots as active materials for PV devices. In this regard, theoretical studies have predicted that the efficiency of graphene-based OSC can reach values as high as 12% by optimizing the opening of the graphene bandgap as well as other cell fabrication and photovoltaic parameters.[47]These calculations encourage to the use of graphene and GQDs as active carbon-based materials for organic photovoltaics.

Despite the potential interest of graphene as light harvesting and active material for PV, no doubt that it can be also used for performing other functions in the PV device. In particular, metallic graphene can form a Schottky junction with a semiconductor and be used as the active layer for solar cells. In addition, due to the graphene nature formed by only one atomic layer, it can be used as transparent electrode for PV, which has demonstrated important advantages over traditional transparent electrodes such as ITO or FTO.[48]

5. Perspectives and outlook

Organic photovoltaic solar cells are currently a broad hot topic in science and, in this regard, some of the known nanoforms of carbon – namely fullerenes, carbon nanotubes as well as graphene and graphene quantum dots – are appealing materials of choice for addressing this issue by efficiently harvesting sunlight and transforming it into other useful forms of energy. In particular, photovoltaics is currently among of the most realistic applications of fullerene derivatives. In contrast, single-wall (SWCNT) and multi-wall (MWCNT) carbon nanotubes are of interest for different applications in the so-called “organic electronics” albeit their use in photovoltaics has not fulfill the expectations so far. In contrast, graphene and chemically modified graphene and graphene quantum dots are promising materials for photovoltaics and a lot of work has been devoted to this study where, for instance, graphene is competing favorably with the well-known and expensive indium-tin oxide (ITO) as transparent electrode.

Special mention should be devoted to the most recent perovskite-based solar cells. Their simplicity in the device preparation and remarkable high energy conversion efficiencies achieved so far, surpassing 20%, have received the attention of the scientific community since it can become a silicon competitor for future solar cell devices. However, perovskites could also

become a strong allied of silicon since recently reported hybrid silicon/perovskite devices have reached efficiency values around 28%.

It is important to note, however, that carbon nanoforms are also an important part in the most recent designs for perovskite devices, both normal and inverted, where they are currently being used as efficient filter for the charges produced in the perovskite layer, as well as electron transporting materials. This is not only a consequence of the favorable morphological interaction between carbon-based materials and perovskites but also to the ease control of the HOMO-LUMO energy levels of the nanoforms of carbon.

Despite the great progress achieved, more efforts are required in order to implement carbon nanomaterials in PV devices. Some of the important issues to address should be mainly focussed on the price, quality and control of the electronic properties of the materials produced. Aspects such as cost and production, material purity, charge mobility and control of the energy levels in the materials involved are essential for improving performances. Whereas this has been achieved in a great extent in fullerenes, this is not still the case for CNTs, despite the great progress achieved during the last few years. Graphene is also affected by the aforementioned drawbacks. In particular, whereas chemical vapor deposition (CVD) growth graphene exhibits remarkable properties in terms of homogeneity and geometrical and electronic quality, this is not the case for the cheaper and readily available graphene produced by exfoliation with solvents (Coleman's method).

The device fabrication is also other challenge so far. In particular, the application of the carbon nanomaterials and the formation of homogeneous films as well as the full control of the interfaces in between the different materials used in the device. Furthermore, although it can be stated that nowadays there is a good understanding on the physical processes involved in the functioning of the photovoltaic solar cell, still there are some open questions, particularly in the interactions of carbon nanomaterials with semiconducting materials, like for instance, in perovskites.

The plastic solar cell concept brings photovoltaic solar energy to a new level. Gathering plastic processing industry and solar energy materials, including carbon-based materials, will have far reaching consequences on the practical application as well as on the production side. In this regard, roll to roll production is well-known in polymer printing technology and its application will modify the current technology in an efficient manner.

This plastic technology, already tested in fullerene derivatives, will not only bring down the cost of produced energy (which is still the major target), but also engage many applications of solar electricity in consumer goods' market which are not accessible up to now due to high cost. Furthermore, this approach enables through semi-transparent photoactive thin film fabrication to access unused large areas other than roofs for photovoltaic energy conversion, such as for instance, windows and walls in buildings. Plastic technology will, eventually, revolutionise not only the photovoltaic industry but also the way of living.

Thus, the aforementioned studies and data clearly provide the answer to the title of this essay in a very positive manner. Far from being a myth, the use of carbon nanostructures for photovoltaic applications is becoming a reality not only from the scientific viewpoint but, most importantly, from a social point of view since the companies around have been able to implement this technology and to produce high-tech devices. Other aspects related with a competitive cost with other forms of energy production, including fossil fuels and other renewable energies, is simple a question of time. In this regard, the strong support given by

some advanced countries like, for instance Germany, with a well-established futuristic plan to remove highly contaminating forms of energy as well as those of high risk, with the challenge of producing 70% of the consumed energy from renewable sources for 2050, paves the way for a safer and clean world and provides a transition to a green and sustainable future, thus giving a solution to energy demanding as the biggest problem facing mankind.

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